

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : G03C 1/492, C08F 4/04, 8/32	A1	(11) International Publication Number: WO 00/54105 (43) International Publication Date: 14 September 2000 (14.09.00)
(21) International Application Number: PCT/US00/06314 (22) International Filing Date: 10 March 2000 (10.03.00) (30) Priority Data: 09/268,430 12 March 1999 (12.03.99) US (71) Applicant: ARCH SPECIALTY CHEMICALS, INC. [US/US]; 501 Merritt 7, P.O. Box 4500, Norwalk, CT 06856-4500 (US). (72) Inventors: FOSTER, Patrick; 48 North Court Street, Providence, RI 02903 (US). SLATER, Sidney, George; 20 Teakwood Drive, Cumberland, RI 02864 (US). STEINHAUSLER, Thomas; 20 Teakwood Drive, Cumberland, RI 02864 (US). BLAKENEY, Andrew, J.; 30 Brookside Court, Seekonk, MA 02771 (US). BIAFORE, John, Joseph; 207 Lexington Avenue, Providence, RI 02907 (US). (74) Agent: GREELEY, Paul, D.; Ohlandt, Greeley, Ruggiero & Perle, L.L.P., 9th floor, One Landmark Square, Stamford, CT 06901-2682 (US).		(81) Designated States: JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HYDROXY-AMINO THERMALLY CURED UNDERCOAT FOR 193 NM LITHOGRAPHY		
(57) Abstract The present invention is directed to a thermally curable polymer composition, and a photolithographic substrate coated therewith, the composition comprising a hydroxyl-containing polymer, an amino cross-linking agent and a thermal acid generator. The thermally curable polymer composition may be dissolved in a solvent and used as an undercoat layer in deep UV lithography.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

HYDROXY-AMINO THERMALLY CURED UNDERCOAT FOR 193 NM LITHOGRAPHY

FIELD OF THE INVENTION

The present invention relates to deep UV lithography used in semiconductor manufacturing and more particularly to undercoat layers for chemically amplified bilayer resist systems.

BACKGROUND TO THE INVENTION

Integrated circuit production relies on the use of photolithographic processes to define the active elements and interconnecting structures on microelectronic devices. Until recently, g-line (436 nm) and i-line (365 nm) wavelengths of light have been used for the bulk of microlithographic applications. However, in order to achieve smaller dimensions of resolution, the wavelength of light used for microlithography in semiconductor manufacturing has been reduced into the deep UV regions of 256 nm and 193 nm. The problem with using deep UV wavelengths is that resists used at the higher wavelengths were too absorbent and insensitive. Thus, in order to utilize deep UV light wavelengths, new resist materials with low optical absorption and enhanced sensitivities were needed.

Chemically amplified resist materials have recently been developed through the use of acid-labile polymers in order to meet the above-mentioned criteria. They have shown great promise in increasing resolution. However, chemically amplified resist systems have many shortcomings. One problem is standing wave effects, which occur when monochromatic deep UV light is reflected off the surface of a reflective substrate during exposure. The formation of standing waves in the resist reduces resolution and causes linewidth variations. For example, standing waves in a positive resist have a

tendency to result in a foot at the resist/substrate interface reducing the resolution of the resist.

In addition, chemically amplified resist profiles and resolution may change due to substrate poisoning. Particularly, this effect occurs when the substrate has a nitride layer. It is believed that the N-H bond in the nitride film deactivates the acid at the nitride/resist interface. For a positive resist, this results in an insoluble area, and either resist scumming, or a foot at the resist/substrate interface.

Furthermore, lithographic aspect ratios require the chemically amplified resist layer be thin, e.g., about 0.5 μm , to print sub 0.18 μm features. This in turn requires the resist to have excellent plasma etch resistance such that resist image features can be transferred down into the underlying substrate. However, in order to decrease absorbance of the chemically amplified resist, aromatic groups, such as those in novolaks had to be removed, which in turn decreased the etch resistance.

Utilizing an underlayer or undercoat film that is placed on the substrate before the chemical amplified film is applied can reduce the above-mentioned problems. The undercoat absorbs most of the deep UV light attenuating standing wave effects. In addition, the undercoat prevents deactivation of the acid catalyst at the resist/substrate interface. Furthermore, the undercoat layer can contain some aromatic groups to provide etch resistance.

In the typical bilayer resist process, the undercoat layer is applied on the substrate. The chemically amplified resist is then applied on the undercoat layer, exposed to deep UV light and developed to form images in the chemically amplified resist topcoat. The bilayer resist system is then placed in an oxygen plasma etch environment to etch the undercoat in the areas where the chemically amplified resist has been removed by the development. The chemically amplified resist in a bilayer system typically contains silicon and is thus able to withstand oxygen plasma etching. After the bottom layer is

etched, the resist system can be used for subsequent processing such as non-oxygen plasma etch chemistry which removes the underlying substrate.

Even though the undercoat attenuates standing waves and substrate poisoning, it poses other problems. First, some undercoat layers are soluble to the chemical amplified resist solvent component. If there is intermixing between the top and undercoat layers, the resolution and sensitivity of the top resist layer will be detrimentally affected.

In addition, if there is a large difference in the index of refraction between the chemical amplified resist and the undercoat layer, light will reflect off the undercoat layer causing standing wave effects in the resist. Thus, the index of refraction between the two layers must be matched to minimize reflectivity effects.

Another problem with undercoating layers is that they are sometimes too absorbent because of incorporation of aromatic groups. Some semiconductor manufacturing deep UV exposure tools utilize the same wavelength of light to both expose the resist and to align the exposure mask to the layer below the resist. If the undercoat layer is too absorbent, the reflected light needed for alignment is too attenuated to be useful. However, if the undercoat layer is not absorbent enough, standing waves may occur. A formulator must balance these competing objectives.

In addition, some undercoats have very poor plasma etch resistance to plasma chemistry. The etch resistance of the undercoat should be comparable to the etch rate of novolak resins in order to be commercially viable.

Furthermore, some undercoat layers require UV exposure in order to form cross-links before the radiation sensitive resist topcoat layer can be applied. The problem with UV cross-linking undercoat layers is that they require long exposure times to form sufficient cross-links. The long exposure times severely constrain throughput and add to the cost of producing integrated circuits. The UV tools also do not provide uniform exposure so that some areas of the undercoat layer may be cross-linked more than other

areas of the undercoat layer. In addition, UV cross-linking exposure tools are very expensive and are not included in most resist coating tools because of expense and space limitations.

Some undercoat layers are cross-linked by heating. However, the problem with these undercoat layers is that they require high curing temperatures and long curing times before the top layer can be applied. In order to be commercially useful, undercoat layers should be curable at temperatures below 250° C and for a time less than 180 seconds. After curing, the undercoat should have a high glass transition temperature to withstand subsequent high temperature processing.

Therefore, it is an object of the present invention to provide a thermally curable polymer composition that is useful for an undercoat layer in deep UV lithography. Another object of the present invention is to provide an undercoat layer, which is cured at temperatures less than about 250° C and for a time less than about 3 minutes. It is a further object of this invention to provide an undercoat layer which is insoluble to the top resist's solvent system, minimizes reflectivity effects, and has an etch rate comparable to novolaks.

Other and further objects, advantages and features of the present invention shall become apparent as described below.

SUMMARY OF THE INVENTION

The present invention is directed to a thermally curable polymer composition comprising a hydroxyl-containing polymer, an amino cross-linking agent and a thermal acid generator. The thermally curable polymer composition may be dissolved in a solvent and used as an undercoat layer in deep UV lithography.

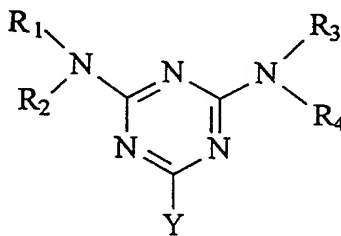
In addition, the present invention also relates to a photolithographic coated substrate comprising: a substrate, a thermally cured undercoat composition on the

substrate, and a radiation-sensitive resist topcoat on the thermally cured undercoat composition. Furthermore, the present invention further relates to a process for using the photolithographic coated substrate for the production of relief structures.

DETAILED DESCRIPTION AND EMBODIMENTS

This invention relates to a thermally curable polymer composition, which may be used for forming an undercoat layer in deep UV lithography. The thermally curable polymer composition comprises a hydroxyl-containing polymer, an amino cross-linking agent and a thermal acid generator and. When the composition is heated, the thermal acid generator protonates the polyfunctional amino cross-linking agent resulting in a very strong electrophilic group. This group reacts with a hydroxyl group on the hydroxyl-containing polymer forming a cured cross-linked polymer matrix.

Any suitable amino cross-linking agent may be used in the present application such as methylolated and/or methylolated and etherified melamines, methylolated and/or methylolated and etherified guanamines and the like. The preferred amino cross-linking agents have the general formula:

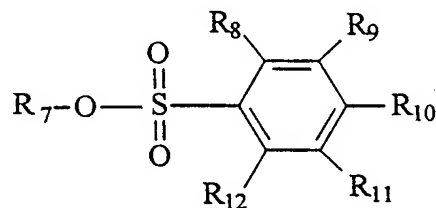


wherein Y is NR_5R_6 or a substituted or unsubstituted aryl or alkyl group; and R_1 to R_6 are independently a hydrogen or a group of the formula $—CH_2OH$ or $—CH_2OR_{17}$ wherein R_{17} is a alkyl group of about 1 to 8 carbons.

Examples of suitable melamine cross-linking agents are methoxyalkylmelamines such as hexamethoxymethylmelamine, trimethoxymethylmelamine, hexamethoxyethylmelamine,

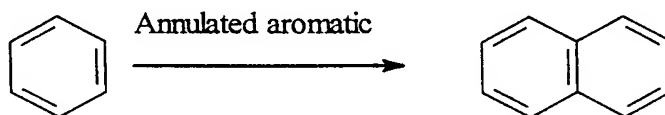
tetramethoxyethylmelamine, hexamethoxypropylmelamine, pentamethoxypropylmelamine, and the like. The preferred melamine cross-linking agent is hexamethoxymethylmelamine.

The thermal acid generator of the present invention has the general formula:



where R_7 is a substituted or unsubstituted alkyl, cycloalkyl or aromatic group wherein the substituted group is a halogen, alkoxy, aromatic, nitro or amino group; and R_8 to R_{12} are independently selected from hydrogen, linear or branched C_1 to C_4 alkyl, alkoxy, amino, alkylamino, aryl, alkenyl, halogen, acyloxy, cycloalkyl, or annulated cycloalkyl, aromatic or heterocyclic. More preferable thermal acid generators are cyclohexyl p-toluenesulfonate, menthyl p-toluenesulfonate and cyclohexyl 2,4,6-triisopropylbenzenesulfonate.

Annulated means that the cycloalkyl, aromatic or heterocyclic ring is connected onto the benzene ring of the thermal acid generator such as, for example, the annulated aromatic shown below



The preferred thermal acid generators are cyclohexyl p-toluenesulfonate, menthyl p-toluenesulfonate, bornyl p-toluenesulfonate, cyclohexyl triisopropylbenzenesulfonate, cyclohexyl 4-methoxybenzene sulfonate.

The thermal acid generators described above should not be considered photoacid generators. Any sensitivity that the thermal acid generators would have to UV light should be very poor, and they cannot practically be used in photolithography as a photoacid generator.

The thermally curable polymer composition also comprises a hydroxyl-containing polymer. Any suitable hydroxyl-containing polymer may be used such as polymers comprising monomer units of cyclohexanol, hydroxystyrene, hydroxyalkyl acrylate or methacrylate, hydroxycycloalkyl acrylate or methacrylate, arylalkyl alcohols, allyl alcohol and the like. This invention also contemplates copolymers, terpolymers, and the like of the foregoing named polymers. In addition, polymers containing novolaks may also be used.

Preferably, polymers comprising monomer units of cyclohexanol, hydroxystyrene, hydroxyalkyl acrylate or methacrylate, arylalkyl alcohols and hydroxycycloalkyl acrylate or methacrylate have a number average molecular weight of about 9000 to 38,000, more preferably 14,000 to 30,000 and even more preferably about 18,000 to 22,000.

In addition, the thermally curable polymer composition may also further comprise monomer units of cycloaliphatic esters of acrylic or methacrylic acid. Suitable examples of monomer units of cycloaliphatic esters of acrylic or methacrylic acid are cyclohexyl acrylate or methacrylate, 4-tert-butylcyclohexyl acrylate or methacrylate and isobornyl acrylate or methacrylate, adamantyl acrylates and methacrylates, dicyclopentenyl acrylates and methacrylates, 2-(dicyclopenteneyloxy)ethyl acrylates and methacrylates and the like. The preferred monomer units of cycloaliphatic ester of acrylic or methacrylic acid are isobornyl acrylate or methacrylate.

Furthermore, the hydroxyl-containing polymer may further comprise aromatic monomer units, preferably styrene or biphenyl acrylate or methacrylate.

Examples of suitable hydroxyalkyl acrylate or methacrylates monomer units are hydroxymethyl acrylate or methacrylate, 2-hydroxyethyl acrylate or methacrylate, 3-hydroxypropyl acrylate or methacrylate, 4-hydroxybutyl acrylate or methacrylate, 5-hydroxypentyl acrylate or methacrylate, and 6-hydroxyhexyl acrylate or methacrylate and the like. Preferably, the hydroxyalkyl acrylate or methacrylate monomer units contains primary hydroxyl groups, although secondary and tertiary alcohol groups or mixtures of primary and secondary or primary, secondary and tertiary alcohol groups may be used. Suitable examples of secondary alcohols are 2-hydroxy-2-methylethyl acrylate or methacrylate, 3-hydroxy-3-methylpropyl acrylate, 4-hydroxy-4-methylbutyl acrylate or methacrylate, 5-hydroxy-5-methyl propyl acrylate or methacrylate, and the like. The preferred hydroxyalkyl acrylate or methacrylate is 2-hydroxyethyl acrylate or methacrylate.

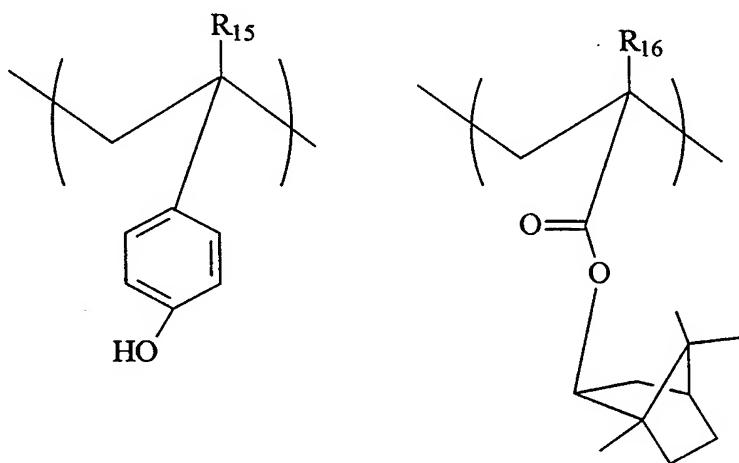
Suitable examples of arylalkyl alcohol monomer units are benzyl alcohol, 4-methyl-benzyl alcohol, 4-ethyl-benzyl alcohol, cumyl alcohol, alpha-methyl benzyl alcohol, 2-phenyl-1-ethanol, 3-phenyl-1-propanol, and 1-naphthyl methanol.

Other preferred copolymers useful in the thermally curable polymer composition are a copolymer of styrene and allyl alcohol monomer units with a weight average molecular weight of about 2000 to 20,000, preferably 2000 to 10,000; and a copolymer of hydroxystyrene and a cycloaliphatic esters of acrylic or methacrylic acid monomer units with a number average molecular weights of about 9000 to 38,000, preferably about 14,000 to 30,000, more preferably about 18,000 to 22,000.

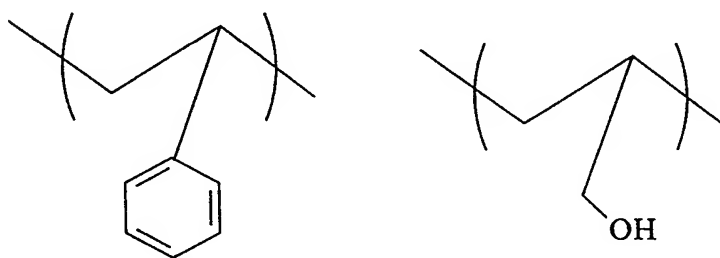
The thermally curable polymer composition preferably contains about 75 to 95 wt. %, and more preferably about 82 to 95 wt. % of hydroxyl containing polymer. The amount of the amino cross-linking agent in the thermally curable polymer composition is preferably about 3 to 20 wt. % and more preferably about 5 to 15 wt. %. The amount of the thermal acid generator in the thermally curable polymer composition is preferably about 0.5 to 5 wt. % and more preferably about 1.5 to 3.5 wt. %.

The thermally curable polymer composition of the present invention should not begin significant cross-linking until it reaches a temperature of about 50° C. Significant cross-linking below 50° C may lead to gel formation at room temperature, which will reduce its shelf life. Gel formation results in non-uniform coatings and linewidth variations across the substrate when the thermally curable polymer composition is used as an undercoat layer in microlithography.

The more preferable polymers of the present invention comprise polymers with the following monomer units:



Polymer 1



Polymer 2

wherein R₁₅ and R₁₆ are independently selected from hydrogen or methyl.

Polymer 1 comprises about 40 to 75 mole % of isobornyl acrylate or methacrylate monomer units and about 25 to 60 mole % of hydroxystyrene monomer units.

Polymer 2 comprises about 39 to 60 mole % of styrene monomer units and about 40 to 61 mole % of allyl alcohol monomer units.

Another preferable polymer (polymer 3) is a copolymer of biphenyl acrylate or methacrylate and hydroxyethyl acrylate or methacrylate. The amount of biphenyl acrylate or methacrylate is about 50 to 90 mole % and the amount of hydroxyethyl acrylate or methacrylate is about 10 to 50 mole %.

The polymerization of the polymers described above may be carried out by any suitable polymerization process such as free radical polymerization. The number average molecular weight of Polymers 1 and 3 are about 9,000 to 38,000, preferably about 14,000 to 20,000 and more preferable about 18,000 to 22,000. The weight average molecular weight of polymer 2 is about 2,000 to 20,000, preferably about 2000 to 10,000.

The present invention also relates to a photolithographic coated substrate comprising: a substrate, a thermally cured undercoat composition on the substrate, and a radiation-sensitive resist topcoat on the thermally cured undercoat composition. The thermally cured undercoat composition comprises the thermally curable polymer composition that comprises a hydroxyl-containing polymer, an amino cross-linking agent and a thermal acid generator which has been heated to form a cross-linked matrix. Any of the polymers described above may be used as the hydroxyl-containing polymer. Preferably, the hydroxyl-containing polymer is selected from Polymers 1 or 2.

The present invention further relates to a process for using the photolithographic coated substrate for the production of relief structures comprising the steps of: providing the photolithographic coated substrate, imagewise exposing the radiation-sensitive resist topcoat to actinic radiation; and forming a resist image by developing the radiation-sensitive resist topcoat with a developer to form open areas in the radiation-

sensitive resist topcoat. In addition, the thermally cured undercoat composition may be removed in the open areas of the developed radiation-sensitive resist topcoat by any suitable process such as oxygen plasma etching to form an image in the thermally cured undercoat composition.

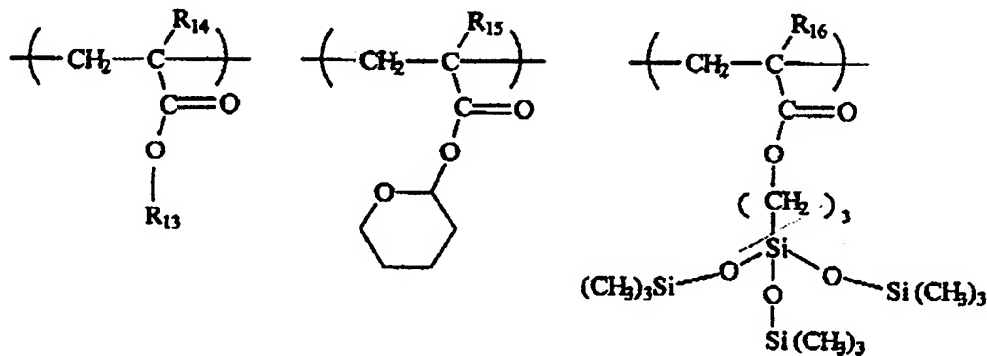
One advantage of the thermally curable polymer composition is that it may be cured at a temperature of less than about 250° C and for a time less than about 180 seconds. This make it particularly useful as an undercoat layer for a resist system where temperature and time constraints are important for commercial viability. Preferably, the thermally curable polymer composition is cured at temperatures between 150 to 250° C and more preferably between temperatures of 180 to 220° C. The preferably curable times are from about 30 to 180 seconds and more preferably from about 60 to 120 seconds.

Both the undercoat and the radiation-sensitive compositions are uniformly applied to a substrate by known coating methods. The compositions are solubilized in an organic solvent and the coatings may be applied by spin-coating, dipping, knife coating, lamination, brushing, spraying, and reverse-roll coating. The coating thickness range generally covers values of about 0.1 to more than 10 μm and more preferably from about 0.1 to 1.5 μm for the radiation-sensitive resist and about 0.3 to 3.0 μm for the undercoat layer. After the coating operation, the solvent is generally removed by curing or drying.

Suitable solvents for both the undercoat and top radiation-sensitive compositions include ketones, ethers and esters, such as methyl ethyl ketone, methyl isobutyl ketone, 2-heptanone, cyclopentanone, cyclohexanone, 2-methoxy-1-propylene acetate, 2-methoxyethanol, 2-ethoxyethanol, 2-ethoxyethyl acetate, 1-methoxy-2-propyl acetate, 1,2-dimethoxy ethane ethyl acetate, cellosolve acetate, propylene glycol monoethyl ether acetate, propylene glycol methyl ether acetate, methyl lactate, ethyl lactate, methyl pyruvate, ethyl pyruvate, methyl 3-methoxypropionate, ethyl 3-methoxypropionate, N-methyl-2-pyrrolidone, 1,4-dioxane, ethylene glycol monoisopropyl ether, diethylene

glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol dimethyl ether, and the like.

The radiation-sensitive resist topcoat of the present invention may be any suitable radiation-sensitive resist. It is typically a chemically amplified resist sensitive to radiation in the deep UV region such as those discussed in U.S. Patent Nos. 5,492,793 and 5,747,622. Preferably, for a bilayer resist system, the radiation-sensitive resist will contain silicon to protect it from oxygen plasma etching. A preferable radiation sensitive resist topcoat comprises a polymer comprising the following monomer units:



wherein R_{13} is methyl or hydroxyethyl, R_{14} is hydrogen, methyl or $\text{CH}_2\text{CO}_2\text{CH}_3$, and R_{15} and R_{16} are hydrogen or methyl, with each choice made independently.

The radiation-sensitive resist will also contain a photoacid generating (PAG) compound. The PAG compounds may be of any suitable type such as sulfonium or iodonium salts, nitrobenzyl esters, imidosulfonates esters and the like. Typically, the PAG will be present in an amount of about 1 to 10% based on the weight of the polymer.

For the production of relief structures, the radiation-sensitive resist is imagewise exposed to actinic radiation. The term 'imagewise' exposure includes both exposure through a photomask containing a predetermined pattern, exposure by means of a computer controlled laser beam which is moved over the surface of the coated substrate, exposure by means of computer-controlled electron beams, and exposure by means of X-

rays or UV rays through a corresponding mask. The imagewise exposure generates acid in the exposed regions of the resist which cleaves the acid labile groups resulting in a polymer which is aqueous soluble. Typically, after imagewise exposure, the chemically amplified resist will be subjected to a post exposure heating treatment that virtually completes the reaction of the photoacid generator with the acid labile groups.

After imagewise exposure and any heat treatment of the material, the exposed areas of the top radiation-sensitive resist are typically removed by dissolution in an aqueous developer. The choice of the particular developer depends on the type of photoresist; in particular on the nature of the polymer resin or the photolysis products generated. The developer can comprise aqueous solutions of bases to which organic solvents or mixtures thereof may have been added. Particularly preferred developers are aqueous alkaline solutions. These include, for example, aqueous solutions of alkali metal silicates, phosphates, hydroxides and carbonates, but in particular of tetraalkylammonium hydroxides, and more preferably tetramethylammonium hydroxide (TMAH). If desired, relatively small amounts of wetting agents and/or organic solvents can also be added to these solutions.

The radiation-sensitive resist used for the bilayer process described above will typically contain silicon or have silicon incorporated into the resist after development. After images are formed in the radiation-sensitive resist, the substrate will be placed in an plasma-etching environment comprising oxygen so that the underlayer coating will be removed. The silicon incorporated in the radiation-sensitive resist forms silicon dioxide when exposed to an oxygen plasma and protects it from being etched so that relief structures can be formed in the undercoat layer.

After the oxygen plasma step, the substrate carrying the bilayer relief structure is generally subjected to at least one further treatment step which changes the substrate in areas not covered by the bilayer coating. Typically, this can be implantation of a dopant, deposition of another material on the substrate or an etching of the substrate. This is

usually followed by the removal of the resist coating from the substrate typically by a fluorine/oxygen plasma etch.

It was surprising and unexpected that the present thermally curable polymer composition worked well as an undercoat layer for lithography with the amino cross-linking agent. There was a concern that the nitrogen bonds in the cross-linking group would deactivate the acid in a positive radiation sensitive resist resulting in an insoluble area, and either resist scumming or a foot at the resist/undercoat interface. However, the following examples showed that the resolution of the resist was excellent and that there was no scumming or foot at the resist/undercoat interface.

This invention is explained below in further detail with references to examples, which are not by way of limitation, but by way of illustration.

EXAMPLE 1

Synthesis Procedure for Polymer 1

In a 100 ml three-necked round bottom flask equipped with a magnetic stir bar, addition funnel, condenser, and nitrogen inlet-outlet was added a mixture of 21.0 g of isobornyl methacrylate, 9.0 g of 4-hydroxystyrene 30 ml of tetrahydrofuran (THF) and 0.45 g of 2,2'-azobis(2-methylbutyronitrile). The mixture was heated to 65°C and stirred for 18 hours. The solution was precipitated by addition to 1 liter of hexanes, and the precipitate was filtered. The solid was dried for 1 hour under a water aspirator vacuum, subsequently dissolved in 80 ml of THF and reprecipitated in 1 liter of hexanes. The precipitate was filtered, and the solid dried at 4 mbar for 24 hours. The yield of polymer was between 77-80%. The above polymer was suspended in a mixture of 70 ml isopropanol, 50 ml THF and 29.5 ml of NH₄OH under a nitrogen atmosphere. After refluxing overnight, the solution was cooled and precipitated by adding 1 liter of water. The suspension was filtered and washed with 50 ml of water and 50 ml of hexanes. The solid was redissolved in THF and precipitated by the addition of 1.2 liter of hexanes. The precipitate was filtered according to the above procedure. The solid was dried at 4 mbar

for 24 hours. Molecular weights and molecular weight distributions were measured using a Waters Corp. liquid chromatograph. The number average molecular weight was 25,923 and the polydispersity (Mw/Mn) was 2.80. Thermal decomposition measurements (TGA) were performed using a Perkin-Elmer thermal gravimetric analyzer (TGA-7) giving a weight loss of 50% between 260-380°C. The structure and composition of polymers was analyzed using a Bruker 250 MHz NMR-spectrometer. The mole % of isobornyl methacrylate was 60% and the mole % of hydroxystyrene was 40%.

EXAMPLE 2

Thermally Curable Polymer Composition using Polymer 1

A 15% by weight thermally curable polymer composition was formulated by combining 2.18g of Polymer 1 from Example 1 above, 0.3g of hexamethoxymethylmelamine and 0.8g of cyclohexyl p-toluenesulfonate in 17 g of propylene glycol methyl ether acetate (PGMEA). The mixture was rolled overnight, and the undercoat solution was filtered twice through a 0.1 µm Teflon filter.

EXAMPLE 3

Thermally Curable Polymer Composition using Polymer 2

A 15% by weight thermally curable polymer composition was formulated by combining 2.18g of Polymer 2 obtained from Scientific Polymer Products, Inc. (60 mole % styrene and 40 mole % allyl alcohol), 0.3g of hexamethoxymethylmelamine and 0.8g of cyclohexyl p-toluenesulfonate in 17 g of propylene glycol methyl ether acetate (PGMEA). The mixture was rolled overnight, and the undercoat solution was filtered twice through a 0.1 µm filter.

EXAMPLE 4

Preparation of Bilayer Resist

A silicon wafer was spin coated with the formulation of Example 1 and baked at 200°C for 1 min to yield a 0.50 μm thick film. A radiation-sensitive resist topcoat was spin coated over the undercoat layer and baked at 100°C for 1 min to yield a 0.25 μm thick film. The radiation-sensitive resist topcoat was a chemically amplified resist system comprising a terpolymer of tetrahydropyranylmethacrylate /methyl methacrylate/ methacryloxypropyl tris(trimethoxy) silane, a triphenylsulfonium-triflate PAG, a triphenylimidole base compound and PGMEA solvent. The coated wafer was then exposed using an ISI 248 nm wavelength stepper. The wafer was post exposure baked at 100° C for 1 min and developed for 30 sec in 0.262 N aqueous TMAH. The wafer was spun dry and the image was analyzed by scanning electron microscopy (SEM). The SEM's showed that there was no scumming or foot at the resist/undercoat interface, no standing waves, and no intermixing of the undercoat and the imaging layer. The bilayer resolution was excellent and could resolve features as small as 0.14 μm in a dense line structure and 0.12 μm for an isolated line structure. In addition, the glass transition temperature of the undercoat was greater than 250° C, which shows that it can withstand subsequent high temperature processing. Furthermore, the oxygen plasma etch rate of the undercoat was within 15% of the etch rate of novolaks.

EXAMPLES 5-12

Preparation and Lithographic Results of Bilayer Resist

Table 1 below shows the lithographic results of different formulations of polymer 1 in Example 2 with an amino cross-linking agent (hexamethoxymethylmelamine) and a thermal acid generator (cyclohexyl p-toluenesulfonate). The formulation and lithographic procedures are the same as Examples 2 and 4.

Table 1

Example	Polymer 1 (grams)	Cross-linking Agent (grams)	Thermal Acid Generator (grams)	PGMEA (grams)	Resolution Dense lines (um)	Resolution Isolated Lines (um)
5	2.75	0.15	0.11	17	0.14	0.13
6	2.60	0.30	0.11	17	0.14	0.13
7	2.70	0.23	0.08	17	0.14	0.12
8	2.81	0.15	0.05	17	0.14	0.13
9	2.41	0.27	0.04	15.4	0.14	0.12
10	3.71	0.68	0.11	25.5	0.15	0.13
11	3.94	0.45	0.11	25.5	0.14	0.12
12	4.16	0.23	0.11	25.5	0.15	0.13

SEM's showed that there were no scumming or foot at the resist/undercoat interface, no standing waves, and no intermixing of the undercoat and the imaging layer.

EXAMPLES 13-14

Preparation and Lithographic Results of Bilayer Resist

Table 2 below the lithographic results of two copolymers of hydroxystyrene and isobornyl methacrylate formulated with the amino cross-linking agent and thermal acid generator described in Examples 5 through 12. The polymer in example 13 contains 55 mole % hydroxystyrene and 45 mole % isobornyl methacrylate. The polymer in example 14 contains 25 mole % hydroxystyrene and 75 mole % isobornyl methacrylate.

Table 2

Example	Polymer (grams)	Cross-linking Agent (grams)	Thermal Acid Generator (grams)	PGMEA (grams)	Resolution Dense lines (um)	Resolution Isolated Lines (um)
13	3.84	0.53	0.13	25.5	0.15	0.13
14	3.84	0.53	0.13	25.5	0.15	0.13

SEM's showed that there were no scumming or foot at the resist/undercoat interface, no standing waves, and no intermixing of the undercoat and the imaging layer.

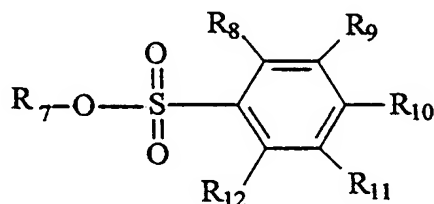
The foregoing is illustrative of the present invention and is not construed as limiting thereof. The invention is defined by the following claims with equivalents of the claims to be included therein.

What is claimed is:

1. A thermally curable polymer composition comprising a hydroxyl-containing polymer, an amino cross-linking agent and a thermal acid generator, wherein said hydroxyl-containing polymer comprises monomer units selected from the group consisting of: cyclohexanol, hydroxystyrene, hydroxyalkyl acrylate or methacrylate, hydroxycycloalkyl acrylate or methacrylate, hydroxyalkylcycloalkyl acrylate or methacrylate, arylalkyl alcohol, and allyl alcohol.

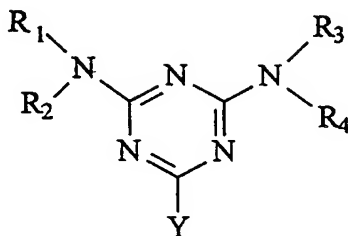
2. The composition of claim 1 wherein said hydroxyl-containing polymer comprises monomer units of cyclohexanol, hydroxystyrene, hydroxyalkyl acrylate or methacrylate, biphenyl acrylate or methacrylate and hydroxycycloalkyl acrylate or methacrylate and has a number average molecular weight between about 14,000 to 30,000.

3. The composition of claim 1 wherein said thermal acid generator has the general structure:



where R_7 is a substituted or unsubstituted alkyl, cycloalkyl or aromatic group wherein the substituted group is halogen, alkoxy, aromatic, nitro or amino group; and R_8 to R_{12} are independently selected from hydrogen, linear or branched C_1 to C_4 alkyl, alkoxy, amino, alkylamino, aryl, alkenyl, halogen, acyloxy, cycloalkyl, or annulated cycloalkyl, aromatic or heterocyclic.

4. The composition of claim 1 wherein said amino cross-linking agent has the general formula:



wherein Y is NR_5R_6 , or a substituted or unsubstituted aryl or alkyl group, R_1 to R_6 are independently a hydrogen or a group of the formula $-CH_2OH$ or CH_2OR_{17} where R_{17} is a alkyl group of about 1 to 8 carbons.

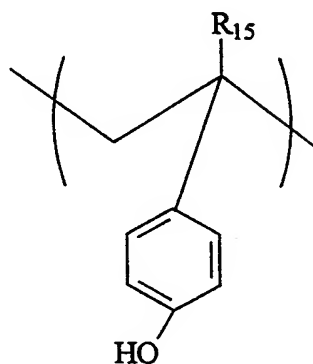
5. The composition of claim 1 wherein said hydroxyl containing polymer comprises a monomer unit of allyl alcohol and has a polymer weight average molecular weight of 2000 to 20000.

6. The composition of claim 1 further comprising a monomer unit of a cycloaliphatic ester of acrylic or methacrylic acid.

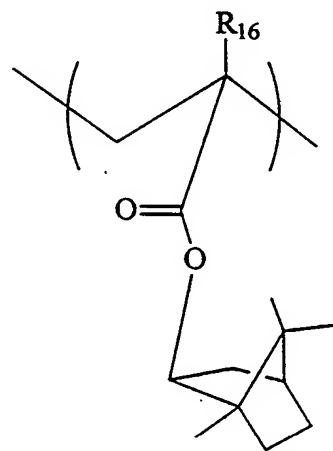
7. The composition of claim 6 wherein said monomer unit of cycloaliphatic ester of acrylic or methacrylic acid is selected from the group consisting of cyclohexyl acrylate, cyclohexyl methacrylates, 4-tert-butylcyclohexyl acrylate, 4-tert-butylcyclohexyl methacrylate, isobornyl acrylate, isobornyl methacrylate adamantyl acrylates and methacrylates, dicyclopentenyl acrylates and methacrylates, 2-(dicyclopenteneyloxy)ethyl acrylates and methacrylates.

8. The composition of claim 1 wherein said hydroxyalkyl acrylate or methacrylate is selected from the group consisting of: hydroxymethyl acrylate or methacrylate, 2-hydroxyethyl acrylate or methacrylate, 3-hydroxypropyl acrylate or methacrylate, 4-hydroxybutyl acrylate or methacrylate, 5-hydroxypentyl acrylate or methacrylate and 6-hydroxyhexyl acrylate or methacrylate.

9. The composition of claim 1 wherein said hydroxyl-containing polymer comprises the following monomer units:



(A)

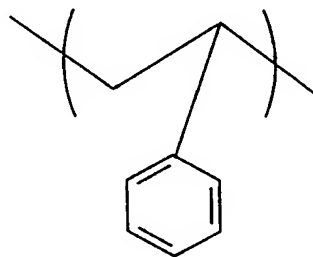


(B)

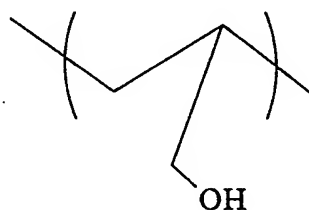
wherein R₁₅ and R₁₆ are independently a hydrogen or a methyl.

10. The composition of claim 9 wherein the mole % of monomer unit (A) is about 25 to 60 mole % and the mole % of monomer unit (B) is about 40 to 75 mole %.

11. The composition of claim 1 wherein said hydroxyl-containing polymer comprises the following monomer units:



(C)



(D)

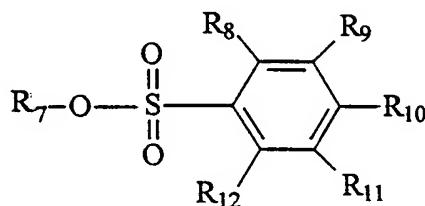
12. The composition of claim 12 wherein the mole % of monomer unit (C) is about 39-60 mole % and the mole % of monomer unit (D) is about 40 to 61 mole %.

13. The composition of claim 3 wherein said thermal acid generator is selected from the group consisting of: cyclohexyl p-toluenesulfonate, menthyl p-toluenesulfonate, bornyl p-toluenesulfonate, cyclohexyl triisopropylbenzenesulfonate, cyclohexyl 4-methoxybenzenesulfonate.

14. A photolithographic sensitive coated substrate comprising:
 (a) a substrate;
 (b) a thermally cured undercoat on the substrate; and
 (c) a radiation-sensitive resist topcoat on the thermally cured undercoat;
 wherein said thermally cured undercoat comprises a thermally cured composition comprising a hydroxyl-containing polymer, an amino cross-linking agent and a thermal acid generator.

15 The coated substrate of claim 14 wherein said hydroxyl-containing polymer comprises monomer units selected from the group consisting of: cyclohexanol, hydroxystyrene, hydroxyalkyl acrylate or methacrylate, hydroxycycloalkyl acrylate or methacrylate, aryalkyl alcohols, and allyl alcohol monomer units.

16. The coated substrate of claim 14 wherein said thermal acid generator has the general structure:



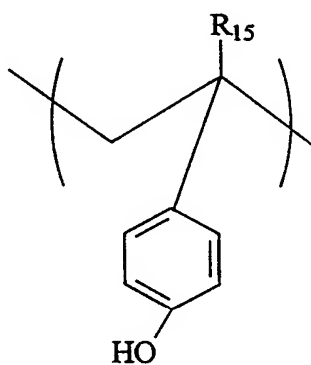
where R₇ is a substituted or unsubstituted alkyl, cycloalkyl or aromatic group wherein the substituted group is halogen, alkoxy, aromatic, nitro or amino group; and R₈ to R₁₂ are

independently selected from hydrogen, linear or branched C₁ to C₄ alkyl, alkoxy, amino, alkylamino, aryl, alkenyl, halogen, acyloxy, cycloalkyl, or annulated cycloalkyl, aromatic or heterocyclic.

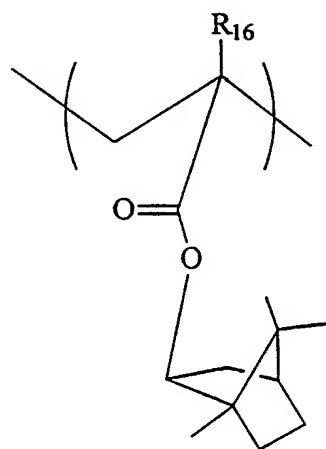
17. The coated substrate of claim 15 wherein said hydroxyl-containing polymer comprises monomer units selected from the group consisting of: hydroxyalkyl acrylate or methacrylate and allyl alcohol units.

18. The coated substrate of claim 14 wherein said hydroxyl-containing polymer further comprises monomer units of cycloaliphatic ester of acrylic or methacrylic acid units.

19. The coated substrate of claim 14 wherein said hydroxyl-containing polymer comprises the following monomer units:



(A)

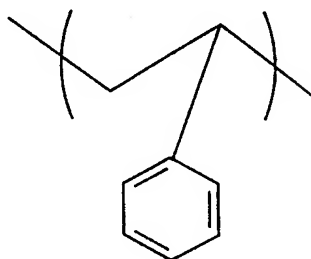


(B)

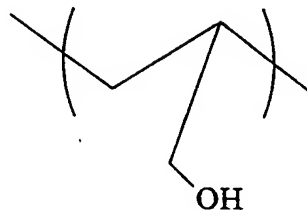
wherein R₁₅ and R₁₆ are independently a hydrogen or a methyl.

20. The coated substrate of claim 19 wherein the mole % of monomer unit (A) is about 25 to 60 mole % and the mole % of monomer unit (B) is about 40 to 75 mole %.

21. The coated substrate of claim 14 wherein said hydroxyl-containing polymer comprises the following monomer units:



(C)



(D)

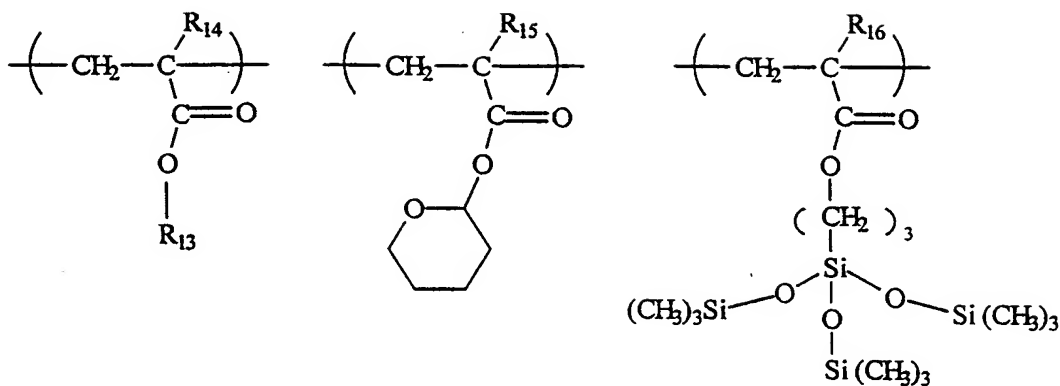
22. The coated substrate of claim 21 wherein the mole % of monomer unit (C) is about 39-60 mole % and the mole % of monomer unit (D) is about 40 to 61 mole %.

23. The coated substrate of claim 14 wherein said hydroxyl-containing polymer comprises biphenyl acrylate or methacrylate and hydroxyethyl acrylate or methacrylate.

24. The coated substrate of claim 23 wherein the amount of biphenyl acrylate or methacrylate is about 50 to 90 mole % and the amount of hydroxyethyl acrylate or methacrylate is about 10 to 50 mole %.

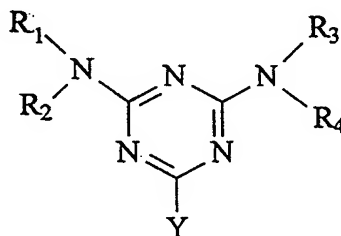
25. The coated substrate of claim 14 wherein the radiation-sensitive resist topcoat is a chemically amplified resist containing silicon.

26. The coated substrate of claim 23 wherein the radiation sensitive topcoat comprises a polymer comprising the following monomer units:



wherein R_{13} is methyl or hydroxyethyl, R_{14} is hydrogen, methyl or $\text{CH}_2\text{CO}_2\text{CH}_3$, and R_{15} and R_{16} are hydrogen or methyl, with each choice made independently.

27. The coated substrate of claim 14 wherein said amino cross-linking agent has the general formula



wherein Y is NR_5R_6 , or a substituted or unsubstituted aryl or alkyl group, R_1 to R_6 are independently a hydrogen or a group of the formula $-\text{CH}_2\text{OH}$ or $\text{CH}_2\text{OR}_{17}$ where R_{17} is a alkyl group of about 1 to 8 carbons.

28. A process for the production of relief structures comprising the steps of:

(a) forming a coated substrate; wherein said coated substrate comprises a substrate; a thermally cured undercoat disposed on said substrate; and a radiation-sensitive resist topcoat disposed on said thermally cured undercoat; and wherein said thermally cured

undercoat comprises a thermally cured composition comprising a hydroxyl-containing polymer, an amino cross-linking agent and a thermal acid generator;

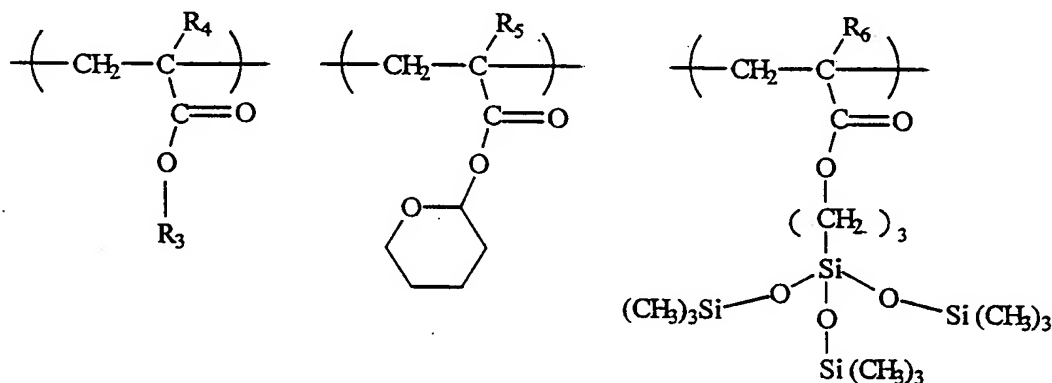
- (b) imagewise exposing said radiation-sensitive resist topcoat to actinic radiation; and
- (c) forming a resist image by developing said radiation-sensitive resist topcoat with a developer.

29. The process of claim 26 wherein said hydroxyl-containing polymer comprises about 30 to 60 mole % of hydroxystyrene monomer units and 40 to 70 mole % of isobornyl acrylate or methacrylate monomer units.

30. The process of claim 26 wherein said hydroxyl-containing polymer comprises about 39 to 60 mole % of styrene monomer units and about 40 to 61 mole % of allyl alcohol monomer units.

31. The process of claim 26 wherein the amount of biphenyl acrylate or methacrylate is about 50 to 90 mole % and the amount of hydroxyethyl acrylate or methacrylate is about 10 to 50 mole %.

32. The process of claim 26 wherein said radiation sensitive resist topcoat comprises a polymer comprising the following monomer units:



wherein R₃ is methyl or hydroxyethyl, R₄ is hydrogen, methyl or CH₂CO₂CH₃ and R₅ and R₆ are hydrogen or methyl, with each choice made independently.

33. The process of claim 26 further comprising the step of:
removing said thermally cured undercoat composition to form an image thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/06314

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :G03C 1/492; C08F 4/04, 8/32

US CL :430/270, 281; 525/328.8, 353, 375, 381, 382

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 430/270, 281; 525/328.8, 353, 375, 381, 382

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,494,777 A (SHIRAKI et al) 27 February 1996, see columns 3 and 5.	1-33
X	US 5,292,614 A (OCHIAI et al) 08 March 1994, see columns 4-6.	1-33

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

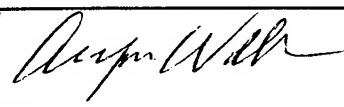
31 MAY 2000

Date of mailing of the international search report

15 JUN 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer - 
BERNARD LIPMAN

Telephone No. (703) 308-0661